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## PATENT SPECIFICATION

NO DRAWINGS

L185,896



Inventor: MAURICE EDWARD CAIN and BRIAN SAVILLE

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International Classification:—C 08 c 5/00; C 08 d 5/02

## COMPLETE SPECIFICATION

## Improvements in or relating to the Treatment of Rubber

We, THE NATURAL RUBBER PRODUCERS' RESEARCH ASSOCIATION, a British Body Corporate, of 19 Buckingham Street, Adelphi, London, W.C.2, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for improving the resistance to degradation of unsaturated natural and synthetic rubbers and to the improved rubbery polymers prepared by the process. More particularly, the invention is concerned with the formation of a rubber-bound anti-oxidant which is formed by the chemical reaction of an aromatic nitroso compound with the molecules of the rubbery polymer.

The oxidative degradation of rubber articles is normally retarded by the addition during compounding, and before vulcanization if employed, of chemicals capable of retarding the reaction of the rubber with oxygen or ozone. These chemicals are most usually phenols or aromatic amines, or combinations of these with or without other functional groups, metal dithiocarbamates, dithiophosphates or other complex compounds. It is an essential feature of their use that they should not undergo chemical reactions during the manufacturing or vulcanization process, and this may be demonstrated by their recovery from the manufactured article by extraction with organic solvents. In applications where the article is at any time in contact with such solvents the resultant loss of the protective agents increases the rate of degradation. In addition, the finite solubility of the commonly used antidegradants in water results in a similar loss during contact with aqueous solutions, reducing the service life of articles such as hoses, hot-water bottles and motor vehicle tyres.

The use of the most efficient amine antidegradants, the substituted *p*-phenylenediamines, is limited to dark-coloured articles since they

discolour badly during ageing and exposure to light. Furthermore even in dark-coloured articles they cannot be used in contact with light-coloured components since the antidegradant will migrate into or on to the surface of the light component and discolour it. For these reasons the less efficient phenolic antidegradants are normally preferred for light coloured articles, especially those produced from rubber latex.

It has now been discovered that efficient antidegradants chemically united with the macromolecules of rubbery polymers may be produced by the reaction between the polymer and a suitably constituted aromatic compound containing a nitroso group attached to one carbon atom of the aromatic ring. In this reaction the nitroso group is converted to a secondary amino group having the polymer molecule as one substituent. By this means may therefore be formed *N,N'*-substituted phenylenediamines, aminophenols, and other antidegradants which are chemically united to the polymer molecules, and cannot be removed even by the most exhaustive extraction procedures.

Since the antidegradants of the present invention are chemically united with the macromolecules of the rubbery polymers, these antidegradants cannot be removed by the action of organic or aqueous solvents and therefore markedly improve the ageing resistance of articles subjected to such action during use. Similarly they are not removed by volatilisation at elevated temperatures and therefore improve high temperature ageing compared to conventional antidegradants, even when contact with solvents is not encountered during the use of the articles. Migration staining of articles in contact with the polymer does not occur because the antidegradant is bound to the polymer molecules.

British Patent Specification No. 785656 concerns a process for pretreating rubbers before compounding and vulcanization by re-

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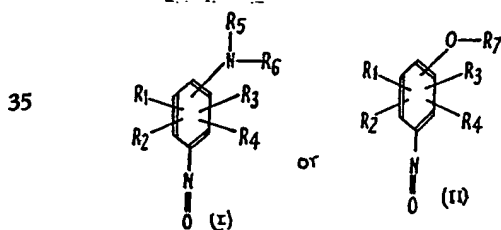
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acting together in the absence of sulphur a vulcanizable rubber and an aromatic nitroso compound. The object of the process is to improve the dispersion of carbon black and other fillers in the rubber, as improved dispersion leads to an improvement in certain dynamic properties of the vulcanizates. The invention is primarily directed at butyl rubbers but is also applicable to unsaturated rubbers.

The process of Specification No. 785656 is a pretreatment effected with prolonged hot milling or working of the reactants during and after reaction. According to one aspect of the present invention, we have found that it is possible to obtain the improved dispersion properties described in the said prior specification, in addition to the rubber-bound antioxidant properties which are the principal object of this invention, during the normal compounding process and without prolonged milling of the reactants together during reaction.

In accordance with the present invention there is provided a process for improving the resistance to degradation of an unsaturated natural or synthetic rubber, which process comprises reacting the rubbery polymer, in the presence of the fillers, additives, vulcanizing agents and other compounding ingredients which are required for the final rubber composition, at least one filler, additive, vulcanizing agent or other compounding ingredient being present during the reaction, with an aromatic nitroso compound having the formula:—



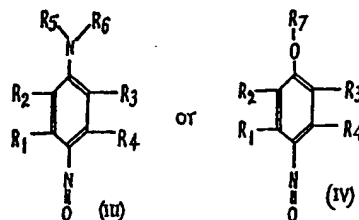
where  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  may be the same or different and each represent a hydrogen atom, a saturated or unsaturated aliphatic (including alicyclic) group or an aryl, aralkyl or alkaryl group which may contain one or more non-carbon atoms, or may, in the case of formula (I) form one or more additional aro-

matic rings fused to the aromatic ring shown in the formula, provided that said groups or aromatic rings are not so large and so positioned as to prevent the functional  $—NR_5R_6$  or  $—OR_7$  group from exerting its antidegradant effect or the reaction of the nitroso compound with the rubbery polymer,

$R_5$ ,  $R_6$  and  $R_7$  may be the same or different and each represent a hydrogen atom, a saturated or unsaturated aliphatic (including alicyclic) group, or an aryl, aralkyl or alkaryl group which may contain one or more non-carbon atoms, or  $R_5$  and  $R_6$  together with the nitrogen atom to which they are attached form a heterocyclic ring which may contain one or more other hetero atoms.

According to a modification of the process described above, the rubber is used dry and the reaction between the rubbery polymer and the aromatic nitroso compound is performed during normal compounding and without prolonged hot milling or working of the reactants together during reaction, but before addition of either the vulcanizing agent or the accelerator or both, and optionally also before addition of certain other fillers, additives and compounding ingredients, as more fully described below.

Preferred aromatic nitroso compounds which may be used in the process of this invention are those which contain the  $—NR_5R_6$  or  $—OR_7$  group in a position *para* to the nitroso group. Such preferred compounds have the following general formulae:—



wherein  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ , and  $R_7$  have the same meaning as defined above.

Examples of specific aromatic nitroso compounds which are preferred for use according to the present invention are as follows:—

Compound	Abbreviation
N,N-dimethyl-p-nitrosoaniline	DMNA
N,N-diethyl-p-nitrosoaniline	DENA
p-nitrosodiphenylamine	NDPA
p-nitrosophenol	NP
2-methyl-4-nitrosophenol	2MNP
3-methyl-4-nitrosophenol	3MNP

The preferred aromatic nitroso compound is p-nitrosodiphenylamine (NPDA) which combines good antioxidant properties with little tendency to migrate from unvulcanized compositions.

As referred to herein the term "rubbery polymer" is intended to include both natural and synthetic polymers containing unsaturated carbon-carbon linkages, or other groups capable of suitable reaction with the compounds of formulae I, II, III and IV above. Rubbery polymers suitable for use in this invention do not include those normally regarded as saturated polymers, which contain very low amounts of unsaturation for vulcanization purposes, for example, ethylene-propylene terpolymers and butyl rubber.

The invention is applicable to rubbery polymers comprising unsaturated natural or synthetic rubbers, in latex or in dry form. Examples of synthetic rubbers which have been successfully treated in dry form are cis-polyisoprene, polybutadiene, styrene-butadiene copolymers, acrylonitrile-butadiene copolymers, and polychloroprene. This rubber-bound antioxidant effect may not easily be obtained with synthetic latices unless alkaline stabilizers are neutralised and vulcanization times are sufficiently long to ensure reaction between the nitroso compound and the rubbery polymer.

Latex compositions may be prepared by mixing solutions or ball-milled dispersions of the aromatic nitroso compound and the other compounding ingredients with the rubber latex, followed by air-drying, coagulation, dipping or foaming by well-known techniques, and finally by reaction between the rubbery polymer and the aromatic nitroso compound during vulcanization.

The present invention provides a simple and effective means of improving the antidegradant properties of articles made from compounded or vulcanized rubbery polymers, particularly under conditions where physical loss of antidegradants occurs by volatilisation or extraction by organic or aqueous solvents. The process is technologically attractive, normally requiring no deviation from standard compounding practice, having only marginal effects on the initial physical properties of the vulcanizates, and being applicable to a wide range of vulcanizing systems. The advantages of rubber-bound antioxidants should be of great importance wherever NR vulcanizates are exposed to constant leaching with water or to dry cleaning or laundering processes. Typical articles benefiting by this invention would be vehicle tyres, steam and water hoses, pipe sealing rings, latex thread, foams, carpet backings, bonded fibres, rubber gloves, diving equipment and swimwear.

In carrying out the process of this invention the aromatic nitroso compound may be mixed with the dry rubbery polymer by any of the usual processes known to the art. It

may be added before, together with, or after such other fillers, additives, vulcanizing agents or other compounding ingredients as may be determined for the subsequent application by the usual practice of the art.

According to one aspect of the invention, the reaction between the aromatic nitroso compound and the rubbery polymer is conducted in the presence of all such added compounding ingredients which are desired for the final rubber composition. Reaction is normally accomplished by heating the two reactants together, for example, at a temperature of from 50°C. to 250°C., preferably from 100°C. to 200°C. for from 60 to 0.5 minutes, higher temperatures requiring shorter reaction times. It will often be convenient to effect this reaction as part of the vulcanization process, but the reaction can be performed prior to vulcanization.

Cold mixing of the rubber with the aromatic nitroso compound and other compounding ingredients may be effected in an open mill with subsequent heating of the mixture to effect reaction. Such cold mixing is effected at temperatures below 100°C., and generally at temperatures of from 40°C. to 70°C.

It is common practice in industry to compound large volumes of rubber in internal mixers. It is usual to masterbatch the rubber, filler, zinc oxide, stearic acid, antioxidant and oil in the internal mixer using high temperatures (100°C. to 180°C.) and short times (2 to 6 minutes, lower times with higher temperatures). We have found that inclusion of the aromatic nitroso compound, particularly NPDA, in the internal mixer, can not only result in the formation of a rubber-bound antioxidant as described above, but can also result in improved dynamic properties of the vulcanizate.

We have found that prolonged hot milling or working of the reactants together during reaction is liable to prevent the formation of the desired rubber-bound antioxidant, and this is particularly true of hot milling at temperatures above about 100°C. An advantage of internal mixers is that dispersion of the compounding ingredients in the polymer matrix may be accomplished in quite a short time without prolonged working. It is therefore preferred that the reaction between the aromatic nitroso compound and the rubbery polymer is effected during the normal mixing of the rubbery polymer and the other compounding ingredients, apart from the vulcanizing agent and/or the accelerator, in an internal mixer. When the vulcanizing agent is added in the internal mixer, a retarding agent is preferably also added to avoid premature vulcanization.

The reaction is preferably effected in the presence of such quantities of fillers pigments and extenders, zinc oxide, stearic acid, processing oils and antidegradants as are desired in the vulcanizate. After reaction, the vulcan-

izing agent and/or the accelerator are preferably added by milling for two or three minutes on an open mill at a temperature of from 40°C. to 70°C. The filler is often some form of carbon black, but silica or whiting or other filler can be used with success instead.

5 The scorch time may be considerably reduced by the incorporation of the aromatic nitroso compound, but this disadvantage can be eliminated or reduced by the addition of a retarder, and/or by the modification of the vulcanizing system. The initial dynamic properties of the vulcanizate are not substantially harmed by the use of aromatic nitroso compounds, and may even be improved under some conditions as indicated above.

10 The rubber-bound antioxidants produced according to this invention will frequently be found to afford complete protection to the rubber composition, making the addition of further antidegradant unnecessary. However, these rubber-bound antioxidants may not confer good fatigue resistance or ozone resistance on the vulcanizate, and further protection may be required if these properties are important.

25 The amount of aromatic nitroso compound used in the process of the invention is pre-

ferably 0.2 to 3.0%, by weight based on the weight of the rubbery polymer, more preferably 0.2 to 0.5%, for latex compositions, 0.5 to 2.0%, for dry rubber compositions. 30

The invention includes a vulcanized unsaturated natural or synthetic rubber whose anti-degradation properties have been improved by the process herein described. The invention also includes a mixture of an aromatic nitroso compound as hereinbefore defined with an unvulcanized unsaturated natural or synthetic rubbery polymer together with such fillers, additives, vulcanizing agents and other compounding ingredients as are required for the final rubber composition, at least one filler, additive, vulcanizing agent or other compounding ingredient being present. 35 40

The following Examples illustrate the manner in which the invention may be carried into effect. All parts are by weight, and given per hundreds parts of dry rubber.  $M_{500}$  is the elastic modulus at 500% extension, T.S. is the ultimate tensile strength, and E.B. the percentage elongation at break. 45 50

In the Examples, abbreviated names are used for the nitroso compounds set out in Table 1.

TABLE 1  
Nitroso compounds


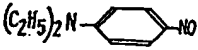
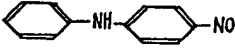

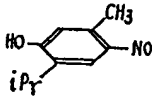

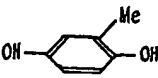
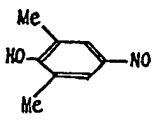
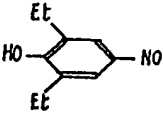
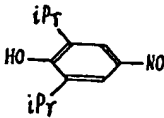
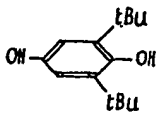
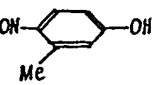
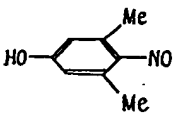
Name	Abbreviation	Structure
N,N-Dimethyl- <i>p</i> -nitrosoaniline	DMNA	
N,N-Diethyl- <i>p</i> -nitrosoaniline	DENA	
<i>p</i> -Nitroso-diphenylamine	NDPA	
<i>p</i> -Nitrosophenol	NP	
6-Nitrosothymol	NT	
<i>p</i> -Nitrosophenyl ethyl ether	NPEE	
2-Methyl-4-nitrosophenol	2MNP	
2,6-Dimethyl-4-nitrosophenol	26DMNP	
2,6-Diethyl-4-nitrosophenol	26DENP	

TABLE 1 (Continued)

## Nitroso compounds

Name	Abbreviations	Structure
2,6-Di-iso-propyl-4-nitrosophenol	26DPNP	
2,6-Di-t-butyl-4-nitrosophenol	26DBNP	
3-Methyl-4-nitrosophenol	3MNP	
3,5-Dimethyl-4-nitrosophenol	35DMNP	

## EXAMPLE 1

The natural rubber compounds shown in Table 2 were prepared by conventional mixing

techniques. The additive was either an aromatic nitroso compound or a conventional anti-oxidant.

TABLE 2  
Natural rubber formulations

	A	B	C	D	E
Purified rubber*	100	100			
Smoked sheet (RSS1)			100	100	100
HAF Black					45
Dutrex R.					5
Zinc oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
N-Cyclohexylbenzothiazole- 2-sulphenamide (CBS)	0.5		0.5		0.5
Sulphur	2.5		2.5		2.5
Tetramethylthiuram disulphide		4		4	
Additive	2	2	2	2	2
Cure time mins/°C.	40/140	60/140	40/140	60/140	40/140

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\*U.S. Rubber Co. Type 2130A, acetone extracted before use.

5 Sheets 0.3 mm. thick were prepared by vul-  
canization as indicated (Table 2) and the oxy-  
gen absorption in pure oxygen at 100°C. and  
the stress relaxation at constant elongation in  
air at 125°C. measured on 10 cm × 0.5 cm  
strips before and after the extraction process.  
This consisted of cold extraction for 24 hours  
under nitrogen with methanol/acetone/chloro-  
10 form azeotrope in a Soxhlet apparatus, fol-

lowed by a similar hot extraction, the solvent  
being removed from the extracted strips by  
pumping at 10<sup>-2</sup> mm. of mercury for 24  
hours. Tables 3 and 4 show the time (T<sub>1</sub>) in  
hours required for the specimens to absorb 1%  
w/w of oxygen, calculated on the total weight  
of vulcanizate, and the time (T<sub>30</sub>) in minutes  
for the loss of 30% of the initial stress.

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TABLE 3  
Oxidation and stress relaxation  
of vulcanizates of Table 2

Additive Table 2		Vulcanizate Table 1	T <sub>1</sub> hours		T <sub>30</sub> minutes	
Type	Identity		Unextracted	Extracted	Unextracted	Extracted
Nitroso	DENA	A	46	*47	155	155
Nitroso	DENA	C	39	30	108	100
Nitroso	DENA	E	30	22	70	**100
Nitroso	NDPA	C	60	53	160	160
Nitroso	NP	C	31	30		
Nitroso	NT	C	30	12		
Conventional	IPPD	A	57	4	110	32
Conventional	IPPD	C	47	4	156	25
Conventional	IPPD	E	40	7	100	25
Conventional	TMQ	C	53	5		
Conventional	BHT	C	47	2		

\*Apparent increase due to normal experimental error.

\*\*This result actually shows an increase in the relevant times after extraction. This unexpected improvement is believed to arise from the removal by the extraction step of pro-oxidant substance such as process oils or catalysts, the effect of which is masked when using conventional antioxidants by the more serious removal of the antioxidants themselves.

IPPD is N-isopropyl-N'-phenyl-p-phenylenediamine.

TMQ is polymerised 2,2,4-trimethyl-1,2-dihydroquinoline.

BHT is 2,6-di-tertiary butyl-p-cresol.

5 The results above clearly demonstrate that the antidegradant effect is retained, and may even be improved, after extraction only by those rubbers prepared using the nitroso compounds.

10 When tetramethylthiuram disulphide (TMTD) is used as the sulphur donor or as an accelerator in vulcanization it is known that an as yet unspecified interaction occurs with a

phenylenediamine type of antidegradant which reduces both the concentration of the latter and the efficiency of the curing system. While DENA or its rubber-bound product undergoes a similar interaction in a TMTD vulcanization the results shown in Table 4 indicate an excellent retention of antidegradant properties even after extraction as previously specified.

15

TABLE 4

Oxidation and stress relaxation of TMTD vulcanizates

Additive	Vulcanizate	T <sub>1</sub> (hours)		T <sub>80</sub> (minutes)	
		Unextracted	Extracted	Unextracted	Extracted
DENA	B	180	150	560	340
DENA	D	155	155	820	480

## EXAMPLE 2

The superior resistance of the aromatic nitroso compound antidegradant to removal by water is demonstrated by comparing the oxida-

tion of two vulcanizates of Example 1 after continuous washing with cold tap water for seven days (Table 5).

TABLE 5

Oxidation of water extracted vulcanizates

Additive	Vulcanizate Table 2	T <sub>1</sub> hours	
		Unextracted	Extracted
DENA	C	39	33
DENA	E	30	32*
IPPD	C	45	8
IPPD	E	39	18

\*Improvement believed to arise from the removal of pro-oxidants by the extraction step in a similar manner to that described with respect to Table 3 above.

## EXAMPLE 3

The effect of an organic solvent (methanol/acetone/chloroform azeotrope) on the protec-

tion afforded by a number of antioxidants has been studied using gum vulcanizates. The formulation used was

Heveacrub SMR 5 L	100
ZnO	5
Stearic acid	2
Sulphur	2.5
N-Cyclohexylbenzothiazole-2-sulphenamide	0.5
Antioxidant	1
Cure time	40'/140°C.

The times required for the absorption of 1% w/w of oxygen before and after extraction by azeotrope as described in Example 1 are shown in Table 6. Conventional antioxidants are com-

pletely removed by the organic solvent, the time to 1% absorption being very close to that of the extracted control sample with no antioxidant added.

TABLE 6

Oxidation of vulcanizates prepared with nitroso compounds of Table 1

Additive	Hours to 1% absorption	
	Unextracted	Azeotrope extracted
None	22	3
DMNA	39	36
DENA	59	42
NDPA	48	59
NP	30	25
NT	32	10
NPEE	29	13
2MNP	32	19
26 DMNP	23	14
26 DENP	28	14
26 DPNP	21	14
26 DBNP	15	5
3 MNP	28	20
35 DMNP	24	9

5 N,N-Dimethyl-*p*-nitrosoaniline (DMNA) provides a further example of the *p*-nitrosoamines, and although slightly less effective in the extracted vulcanizate than the other two examined, nevertheless shows excellent retention of activity after extraction.

10 The seven alkyl substituted 4-nitrosophenols at the end of Table 6 confirm the formation of network-bound antioxidants from this class of compound generally, but show that the effectiveness is reduced if bulky substituents

are present in the 2,6 positions or if both the 3 and 5 positions are substituted.

## EXAMPLE 4

15 In Example 1 above the various dry rubber formulations were made up with 2 parts of additive per 100 parts of rubber. The following Table 7 shows the results of experiments using various parts of DENA in vulcanizate C of Table 2: 20

TABLE 7

DENA parts	T <sub>1</sub> hours	
	Unextracted	MAC extracted
0.3	31	—
1.0	37	37
2.0	39	30

The above Table indicates an optimum level of about 1 part for gum vulcanizates.

#### EXAMPLE 5

##### Effect of variation of filler

- 5 Previous Examples have used carbon black as filler. The following results indicate the

effect of using either silica or whiting. The formulation used was identical with that of vulcanizate E of Table 2, but the fillers were incorporated at the level of 30 parts per 100 parts by volume of rubber. The times to 1% w/w oxygen absorption at 100°C. are shown in Table 8.

10

TABLE 8

Effect of variation of filler

Filler	Additive	Hours to 1% absorption at 100°	
		Unextracted	Extracted
Silica	None	40	16
Silica	NDPA	77	73
Whiting	None	17	4
Whiting	NDPA	57	54

- 15 The formation of the rubber-bound anti-oxidant in the presence of these fillers is thus confirmed.

#### EXAMPLE 6

Synthetic rubber vulcanizates were prepared from a variety of polymers according to the formulations shown in Table 9.

20

TABLE 9

	F	G	H	I	J
Styrene-butadiene copolymer (Intol 1500)	100				
Polybutadiene (Intene 55NF)		100			
Polychloroprene (Neoprene WRT)			100		
Acrylonitrile-butadiene (Krynac 803)				100	
cis-Polyisoprene (Natsyn 400)					100
HAF black	50	50			50
SRF black			50	50	
Dutrex R (processing oil)	8	8			5
Zinc oxide	5	5	5	5	5
Magnesium oxide			4		

TABLE 9 (Continued)

	F	G	H	I	J
Stearic acid	3	3	1	1	2
Coumarone resin				5	
CBS	1.5	1.5			0.5
Mercaptobenzthiazole				1	
Sulphur	1.5	1.5			2.5
MC Sulphur				1.5	
Ethylene thiourea			0.5		
Additive	2	2	2	2	2
Cure time min/°C.	30/153	30/153	30/150	40/180	50/140

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The time taken for these vulcanizates to absorb 1% of oxygen, both before and after extraction, was measured as described in Example 1. The results are given in Table 10. 5

TABLE 10

Network-bound antioxidants in synthetic rubbers. Oxidation at 125°C.

Rubber	Additive	Hours to 1% oxygen absorption	
		Unextracted	Extracted
Styrene-butadiene	IPPD	36	16
	NDPA	38	33
Polybutadiene	IPPD	25	11
	NDPA	25	31
Polychloroprene	PBN	91	23
	NDPA	55	50
Acrylonitrile-butadiene	NA	48	15
	NDPA	84	39
cis-Polyisoprene*	IPPD	69	10
	NDPA	59	54

\*Oxidation at 100°C.

PBN is phenyl-beta-naphthylamine.

NA is an aldol-alpha-naphthylamine condensate.

**EXAMPLE 7**  
Various amounts of DENA were introduced as a 50% aqueous ball-milled dispersion into

natural rubber latex (QLA) which was then compounded as shown in Table 11.

5

TABLE 11

Natural rubber latex compounds

	K	L	M	N	P	Q
Rubber	100	100	100	100	100	100
Zinc oxide	1	2	1	6	5	1
Zinc diethyldithiocarbamate	1	1	1	1	1	1
Sulphur	1		1	1	2.5	1
Tetramethylthiuram disulphide		3				
Zinc mercaptobenzthiazole		1	1		1	
Thiourea		1				
Cure/mins/°C.	30/100	30/100	30/100	30/100	30/100	Varies

Films (ca. 1 mm thick) were prepared by evaporation and cured, and portions of compounds K and L subjected to hot Soxhlet extraction for 6 hours with a methanol acetone/chloroform azeotrope, dried *in vacuo* and aged

10

alongside unextracted film. The physical properties are shown in Table 12, which clearly demonstrates the remarkable ageing resistance after extraction of these vulcanizates prepared according to this invention.

15

TABLE 12

Physical properties of latex vulcanizates of Table 11

Vulcanizate (Table 11)	DENA parts	Unextracted/unaged			Extracted/aged 1 day at 100°		
		T.S.	E.B.	M <sub>500</sub>	T.S.	E.B.	M <sub>500</sub>
	0	350	930	24	Untestable		
K	0.3	330	880	28	100	700	24
	1.0	320	820	32	185	720	40
	0	305	885	39	16	780	6
L	1.0	265	830	38	245	850	31

**EXAMPLE 8**

A further example of the use of a nitroso-phenol in air-dried latex films makes use of DMNP. The films were cured at 100°C. in air for 1 or 5 hours. In this case the films obtained after vulcanization for 1 hour at 100° were lighter in colour than those obtained using either DENA or NDPA. DBNPD is an

20

25

abbreviation for N,N'-di-beta-naphthyl-paraphenylenediamine in this and the following examples. The results of technological tests on azeotrope extracted samples show (Table 13) clearly the superiority of the network-bound antioxidant at both cure times. Additive concentration was 1% of the rubber solids.

30

TABLE 13

Ageing of extracted latex films

Compound	Additive	Cure time (hrs.)	Unaged properties			Aged 2 days at 100°C.		
			T.S.	E.B.	M <sub>500</sub>	T.S.	E.B.	M <sub>500</sub>
Q	DBNPD	1	320	800	43	17	540	14
Q	26 DMNP	1	320	715	82	64	620	36
Q	DBNPD	5	320	775	48	40	630	18
Q	26 DMNP	5	280	620	125	100	550	73

## EXAMPLE 9

*Dipped films*

Technological test results (Table 14) have  
 5 been obtained in films produced from com-

pound M (Table 11) by coagulant dipping  
 followed by acid leaching. The additives used  
 were DBNPD and the nitroso compound  
 NDPA, each in an amount of 0.5%.

TABLE 14

Network-bound antioxidants in dipped latex films

Additive	Treatment	Unaged			Aged 1 day at 100°C.		
		T.S.	E.B.	M <sub>500</sub>	T.S.	E.B.	M <sub>500</sub>
DBNPD	Unextracted	295	860	32	140	580	68
DBNPD	Extracted	280	815	38	*	*	*
NDPA	Extracted	380	880	39	200	910	22

\*untestable.

## EXAMPLE 10

The physical properties of vulcanizates prepared in the form of air-dried films from compound N of Table 11, before and after azeo-  
 15 trope extraction, are set out in Table 15.

The extracted films containing the rubber-bound antioxidants still show better retention of properties after one day at 100°C. than the unextracted films containing twice as much of the conventional antioxidant DBNPD.

20

TABLE 15  
Heat ageing of latex vulcanizates

Property	Days at 100°	Control	Unextracted			Control	Extracted		
			DBNPD 0.5	DENA 0.25	NDPA 0.25		DBNPD 0.5	DENA 0.25	NDPA 0.25
Tensile strength (kg/cm <sup>2</sup> )	0	366	362	364	374	375	380	372	366
	1	247	262	269	267	18	36	284	290
	3	214	230	231	250	*	*	17	150
Elongation at break	0	850	830	810	810	875	890	830	830
	1	847	845	670	640	780	870	850	865
	3	820	730	660	680	*	*	540	820
Modulus at 500% (kg/cm <sup>2</sup> )	0	31	34	40	41	35	35	40	41
	1	27	40	65	65	6	7	31	32
	3	26	41	63	68	*	*	15	24

\*Untestable

#### EXAMPLE 11

Latex foams containing NDPA or DBNPD were prepared from compound P of Table 11. The initial brown colour of the nitroso compound disappeared almost completely during vulcanization, giving a foam only fractionally darker than the conventional one. Oxygen

absorption measurements on thin strips of the two foams are set out below in Table 16. They show that the ageing resistance of the two strips is similar before azeotrope extraction, and that only the conventional antioxidant is removed by this treatment.

TABLE 16

Additive 1%	T <sub>1</sub> hours	
	Unextracted	Extracted
DBNPD	71	7
NDPA	57	60

#### EXAMPLE 12

This Example shows the effects of milling the ingredients during reaction. The formula-

tion and mixing procedure are those described in Example 9 of British Patent Specification No. 785656, as follows:

10

20



	Parts by weight
Smoked sheet (RSS1)	100
p-Nitrosophenol	2
MPC Black	50
Zinc oxide	5
Sulphur	2.5
Mercaptobenzthiazole	1
Phenyl- $\beta$ -naphthylamine	1

5 The rubber, stearic acid and p-nitrosophenol were mixed on a cool mill at 68°C. and then hot milled for 10 minutes at 155°C. The carbon black was added and mixed on the mill at about 68°C., and then milled for 5 minutes at 155°C. Considerable difficulty was experienced in carrying out this operation as the rubber became extremely soft and did not easily band on the mill. The remaining ingredients were added on the mill at 68°C. and the compositions cured at 142°C. for 65 minutes.

15 A control sample in which the p-nitrosophenol was omitted at the first stage was also prepared. To some of this control sample 2 parts of p-nitrosophenol was added after compounding on a cold mill at 40°C. in accordance with the process of the present invention.

20 The three vulcanizates tested were therefore

R Control, heat-treated without p-nitrosophenol

S Heat-treated with p-nitrosophenol

25 T Heat-treated without p-nitrosophenol, but p-nitrosophenol added in cold after compounding.

#### Dynamic Tests

Samples in the form of 1 in.  $\times$  0.7 in. diameter cylinders were subjected to dynamic testing to measure the change in in-phase shear modulus with strain amplitude. The value of this modulus change over a double strain amplitude range of 0.001 to 1.0 decreases considerably as the dispersion of the filler improves, smaller values indicating the success of the heat-treatment process.

#### Oxygen Absorption Tests

The times required for the absorption of 1% w/w oxygen at 100°C. under 760 mm. of pure oxygen were measured on samples cut from 10 cm  $\times$  10 cm  $\times$  0.3 mm vulcanized sheets before and after extraction by organic solvents. The extraction process consisted of continuous Soxhlet extraction with cold methanol/acetone/chloroform azeotrope for 24 hours, followed by similar extraction with hot azeotrope. The samples were dried by pumping at  $10^{-2}$  mm. Hg. for at least 24 hours.

Results are given in Table 17.

TABLE 17

Sample	Dynamic Shear Modulus Change (dynes/cm <sup>2</sup> ) $\times 10^7$	Hours to 1% oxygen absorption	
		Unextracted	Extracted
R	0.552	37	9
S	0.164	42	11
T	1.348	40	36

#### Conclusions

55 The process of Specification No. 785656 using p-nitrosophenol with high-temperature milling (S) gives a considerable improvement

in dynamic properties over the purely thermal process (R), which itself is an improvement on a normally compounded rubber which normally gives a modulus change of the order of 1.4

5  $\times 10^7$  dynes cm.<sup>-2</sup>. However, the improvement in oxygen absorption after extraction is not very large. The rubber-bound antioxidant is most effective when formed as in vulcanizate T whereas the improvement in dynamic properties is lost in this case. These results clearly show that the effects of the two processes, i.e. with or without milling during reaction are completely different.

## EXAMPLE 13

10 This Example shows how an improvement of both dynamic properties and rubber-bound antioxidant properties may be achieved by the use of an internal mixer without any mixing or heating steps other than those which are normally necessary for compounding rubber. 15 Compounds were formed from the compositions given in Table 18.

TABLE 18

	U	V	W	X	Y	Z
Heveacrub SMR5	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
HAF black	45	45	45	45	45	45
Dutrex R	5	5	5	5	5	5
NDPA	0	2	0	2	0	2
N-nitrosodiphenylamine (retarder)	0.5	1	0	0	0	0
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5
CBS	0.5	0.5	0.5	0.5	0.5	0.5

20 Compounds U and V were prepared by adding all the ingredients, except the CBS accelerator, together to a Banbury internal mixer at 50°C., mixing for 3 minutes with water on throughout the mixing cycle, and 25 dumping at 140°C. to 150°C. (The retarder was included to prevent premature vulcanization). The accelerator was added with milling for 2 or 3 minutes on an open mill at 40°C. to 50°C.

30 Compounds W and X were prepared by adding all the ingredients except the sulphur and the accelerator, together to a Banbury internal mixer at 100°C., mixing for 3 minutes, and dumping at 170°C. The sulphur and the accelerator were added by milling for 2 or 3 minutes on an open mill at 40°C. to 50°C. 35

Compounds Y and Z were prepared in a Banbury internal mixer starting at 50°C. according to this time cycle 40

0 minutes	Add the rubber (to masticate).	
3 minutes	Add zinc oxide, stearic acid, NDPA.	
4 minutes	Add half the HAF black	
6 minutes	Add the oil and the rest of the black.	45
8 minutes	Dump (temperature measured as 150°C.)	

The sulphur and the accelerator were added by milling for 2 or 3 minutes on an open mill at 40°C. to 50°C. 50

All mixes were cured for 40 minutes at 140°C. Dynamic and oxidation properties are given in Table 19.

TABLE 19

Vulcanizate	Dynamic Shear Modulus Charge (dynes/cm <sup>2</sup> ) $\times 10^7$	Hours to 1% oxygen absorption	
		Unextracted	Extracted
U	0.72	32	7
V	0.15	45	50
W	0.656	17	6
X	0.256	39	47
Y	1.113	17	6
Z	0.227	42	56

## EXAMPLE 14

NPDA was chosen for technological evaluation in comparison with one of the best conventional antioxidants, IPPD. A tyre tread compound was used for this purpose, which was compound E of Table 2, except that Heveacrub SMR5 was used in place of Smoked Sheet RSS1. As NPDA was difficult to disperse in gum compounds below 70°C, it was added to the black masterbatch at this temperature. The use of higher temperatures was avoided to prevent premature reaction of the nitroso compound with the rubber, which led to some peptising action.

The results of air oven ageing tests at 100°C. on the vulcanizates before and after extraction are given in Table 20. The rubber-bound antioxidant gives protection comparable to that of IPPD in the unextracted vulcanizates. Azeotrope extraction reduces the ageing resistance of the vulcanizates containing IPPD almost to the level of the control, whereas it actually improves the protection given by the rubber-bound antioxidant. The continuing increase in modulus on ageing shown at the higher levels of both IPPD and NDPA is characteristic of vulcanizates containing p-phenylenediamines.

TABLE 20  
Heat ageing of tyre-tread vulcanizate

Property	Unextracted		IPPD			NDPA		
	Days at 100°	Control	0.5	1	2	0.5	1	2
Tensile strength (kg/cm <sup>2</sup> )	0	272	282	290	287	248	252	255
	1	190	216	231	210	194	184	220
	3	70	71	83	99	69	87	88
Elongation at break (%)	0	470	490	495	510	420	435	430
	1	360	380	380	380	380	310	330
	3	210	210	195	185	190	190	145
Modulus at 100% (kg/cm <sup>2</sup> )	0	31	33	33	28	31	30	30
	1	35	38	42	36	39	40	41
	3	27	31	36	46	32	39	53
Tensile strength (kg/cm <sup>2</sup> )	0	270	279	274	255	250	242	253
	1	95	122	135	125	195	208	209
	3	30	41	47	42	77	148	156
Elongation at at break (%)	0	440	450	435	430	405	395	395
	1	260	275	275	245	305	315	285
	3	95	135	145	120	185	225	195
Modulus at 100% (kg/cm <sup>2</sup> )	0	33	34	32	29	30	29	31
	1	25	33	32	33	38	40	43
	3	—	29	28	35	34	47	59

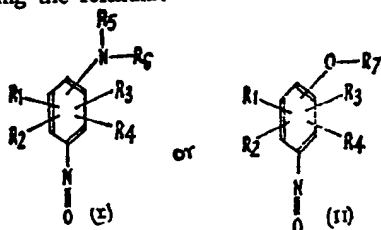
The results of abrasion resistance tests of the vulcanizates before extraction, and after either azeotrope extraction as described in Example 1 or water extraction by leaching for two weeks continuously with cold running tap water at ambient temperatures, are given in Table 21. The results are expressed relative to the results obtained with no antioxidant.

TABLE 21

Relative Akron abrasion index (control as 100)	None	Additive (parts phr)			NDPA		
		IPPD					
Unextracted	100	0.5	1	2	0.5	1	2
Azeotrope extracted	100	153	143	172	120	150	157
Water extracted	100	111	100	131	123	137	184
	100	126	120	144	130	148	185

## WHAT WE CLAIM IS:—

1. A process for improving the resistance to degradation of an unsaturated natural or synthetic rubber, which process comprises reacting the rubber polymer, in the presence of the fillers, additives, vulcanizing agents and other compounding ingredients which are required for the final rubber composition, at least one filler, additive, vulcanizing agent or other compounding ingredient being present during the reaction, with an aromatic nitroso compound having the formula:—



- where  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  may be the same or different and each represent a hydrogen atom, a saturated or unsaturated aliphatic (including alicyclic) group or an aryl, aralkyl or alkaryl group, which may contain one or more non-carbon atoms, or, in the case of formula (I), may form one or more additional aromatic rings fused to the aromatic ring shown in the formula, provided that said groups or aromatic rings are not so large and so positioned as to prevent either the functional  $—NR_5R_6$  or  $—OR_7$  group from exerting its antidegradant effect or the reaction of the nitroso compound with the rubbery polymer,

- $R_5$ ,  $R_6$  and  $R_7$  may be the same or different and each represent a hydrogen atom, a saturated or unsaturated aliphatic (including alicyclic) group, or an aryl, aralkyl or alkaryl group which may contain one or more non-carbon atoms, or  $R_5$  and  $R_6$  together with the nitrogen atom to which they are attached form a heterocyclic ring which may contain one or more hetero atoms.

2. A modification of the process claimed in claim 1, wherein the rubber is used dry and the reaction between the rubbery polymer and the aromatic nitroso compound is performed during normal compounding and without prolonged hot milling or working of the reactants together during reaction, but before addition of either the vulcanizing agent or the accelerator or both, and optionally also before addition of certain other fillers, additives and other compounding ingredients.

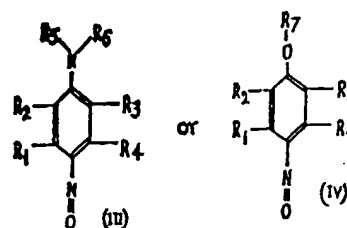
3. A process as claimed in claim 2, wherein the reaction between the aromatic nitroso compound and the rubbery polymer is effected during normal mixing of the rubber and the other compounding ingredients apart from the vulcanizing agent and/or the accelerator, in an internal mixer.

4. A process as claimed in claim 2 or claim 3, wherein reaction between the aromatic nitroso compound and the rubbery polymer is effected in the presence of such quantities of fillers extenders and pigments, zinc oxide, stearic acid, processing oils and antidegradants as are required in the vulcanizate.

5. A process as claimed in any one of claims 2 to 4, wherein the vulcanizing agent and/or the accelerator are added, after reaction between the aromatic nitroso compound and the rubbery polymer has been effected, with milling for two or three minutes on an open mill at a temperature of from  $40^\circ\text{C}$ . to  $70^\circ\text{C}$ .

6. A process as claimed in claim 1, wherein the rubbery polymer is used in the latex state, and the aromatic nitroso compound is added in the form of a solution or ball-milled dispersion in a suitable solvent before, after or together with solutions or ball-milled dispersions of such fillers, pigments, antidegradants, vulcanizing ingredients and other compounding ingredients as required in the final vulcanizate.

7. A process as claimed in any one of claims 1 to 6, wherein the aromatic nitroso compound has the formula:—



- where  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ , and  $R_7$  have the meanings defined in claim 1.

8. A process as claimed in claim 7, wherein the aromatic nitroso compound is p-nitroso-phenylamine.

9. A process as claimed in any one of claims 1 to 8, wherein the proportion of the aromatic nitroso compound is from 0.2% to 3.0% of the weight of the rubbery polymer.

10. A process as claimed in claim 9, wherein the rubbery polymer is used dry and the proportion of the aromatic nitroso compound is from 0.5% to 2.0% of the weight of the rubbery polymer.

11. A process as claimed in claim 9, wherein the rubbery polymer is used in the form of a latex and the proportion of the aromatic nitroso compound is from 0.2% to 0.5% of the weight of the rubbery polymer.

12. A process as claimed in any one of claims 1 or 7 to 11, wherein the reaction between the rubbery polymer and the aromatic nitroso compound is performed during the vulcanization step.

13. A process as claimed in any one of claims 1 to 12, wherein a vulcanization retarder is included in the mixture.

14. A process as claimed in claim 1 or claim 2, and substantially as hereinbefore described in any one of the Examples.

5 15. A vulcanized unsaturated natural or synthetic rubber whose antidegradation properties have been improved by the process claimed in any one of claims 1 to 14.

10 16. A mixture of an aromatic nitroso compound as defined in claim 1 with an unvulcanized unsaturated natural or synthetic rub-

bery polymer together with such fillers, additives, vulcanizing agents and other compounding ingredients as are required for the final rubber composition, at least one filler, additive, vulcanizing agent or other compounding ingredient being present. 15

STEVENS LANGNER, PARRY &  
ROLLINSON,  
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Agents for the Applicants.

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